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SPECTROSCOPIC DIAGNOSTICS TO SUPPORT
ADVANCED MICROELECTRONIC
FABRICATION TECHNIQUES

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This is the first annual report on a program to develop laser spectroscopic diagnostics for detection of gas phase species important in fabrication processes for advanced semiconductor materials. It has two objectives, to obtain quantitative spectroscopic data for these molecules, and to apply diagnostics to model fabrication systems. This report summarizes progress in the areas of investigation identified in the first year: chlorine atom detection using an infrared tunable diode laser, which will also be used to instrument a plasma etching reactor, and infrared and laser induced fluorescence spectroscopic studies of SiF_2 , CF_2 , and SiH_2 .					
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1. INTRODUCTION

1.1 Research Objectives

This is the first Annual Report on AFOSR Contract F49620-84-C-0036, "Spectroscopic Diagnostics to Support Advanced Microelectronic Fabrication Techniques." This is a program to develop laser spectroscopic diagnostics for detection of gas phase species important in fabrication processes for advanced semiconductor materials.

Its objectives are two-fold:

- o To provide basic spectroscopic data for a number of the small molecules which play important roles in semiconductor fabrication processes,
- o To instrument model fabrication systems with spectroscopic diagnostics in order to characterize important gas phase species concentrations or concentration profiles under actual operating conditions.

This experimental program makes extensive use of the tunable infrared diode laser, tunable dye laser, and flow tube reactor facilities available at Aerodyne Research, Inc., for the study of quantitative spectroscopy of radical species. Close cooperation with research and development groups in these fields is planned, both to confirm which systems and molecular species are of most interest, and to work toward the instrumentation of model apparatus. The program plan was that after an appropriate apparatus was identified or constructed at Aerodyne, planning of the diagnostics would begin towards the end of the first year of the program, with construction and diagnostic measurements coming in the second and third years. In fact, in this first year we have not only identified an excellent system for collaborative measurements, but have designed and obtained the required optical system and

are anticipating measurements in a few months. Preliminary measurements have also been made in our laboratory on a number of molecular systems. In the rest of this section, we will discuss our choice of systems, describing their importance and our goals in each area. The following section will summarize progress in each investigation.

1.2 Systems Under Study

The laser diagnostics described in this report will be most useful in laboratory studies directed toward understanding the physics and chemistry involved in the various semiconductor fabrication processes. However, in many cases, they can also be applied to process monitoring, since control of gas-phase concentrations is often critical to the success of the process. The systems of interest can be divided into several broad areas. Each area is characterized by its own important molecular species, its own outstanding mechanism questions and needs for further investigation, and its own requirements for continuous monitoring. The semiconductor fabrication techniques to which spectroscopic diagnostics can be applied include plasma etching and chemical vapor deposition (CVD) and plasma deposition. We will discuss each in turn.

Plasma etching is an important and widely used semiconductor processing technique. In this process, the plasma discharge dissociates a stable gas, for example CF_4 , into etchant species, here F atoms and CF_x radicals. These attack the semiconductor substrate, for example silicon, to generate volatile species. In the case of silicon, SiF_4 is the final product, although the identity of the actual desorbing species is still open to question. Other unresolved questions relating to mechanisms include the reasons for selectivity in etching between silicon and silicon dioxide (a desirable trait for generating patterns in layered semiconductor films), the effects of hydrogen and oxygen addition on this selectivity, and the causes of anisotropic etching (another desirable trait, since when etch rates into the surface are much larger than those parallel to it, circuit patterns can be

made much closer together). Species of interest in these systems include both etching radicals, especially halogen atoms, and desorbing species, which in silicon etching may include SiF_x radicals. The last few years have seen very substantial experimental and theoretical investigations,¹⁻⁷ yet questions remain.

As a candidate for inclusion in the applications phase of this program, measurement of halogen atom concentrations in a laboratory plasma etching system ranked high on our list for two reasons. The first is that these atomic species are thought to be the chief, if not only, reactions with the surface leading to etching so that correlating absolute number densities and concentration profiles with observations of etch rate and plasma parameters can substantially increase understanding of etching systems. The second reason is that we have had considerable experience in the measurement of fluorine atom concentrations, including the first measurement of the $^2\text{P}_{1/2} + ^2\text{P}_{3/2}$ transition lifetime,⁸ measurement of pressure broadening parameters,⁹ and the development of a dedicated diagnostic apparatus for concentration measurements in advanced chemical lasers.

Therefore, we were particularly fortunate in making contact with Prof. Herbert H. Sawin of the MIT Chemical Engineering Department (initially at a Gordon Conference on Plasma Chemistry attended by J. Wormhoudt). Prof. Sawin had been taking data on chlorine etching systems (Cl_2 and ClF_3 etch gases and silicon substrates) using quadrupole mass spectrometric ion and neutral detection, diode array optical emission spectra, laser interference thickness monitoring, and accurate plasma current and voltage measurements to infer quantities such as electron density. His measurements, which were made as a function of parameters such as discharge frequency, were pointed toward development of first a steady-state and eventually a dynamic model of the plasma. In addition, he had designed his apparatus with three additional optical ports accessing the etching region and with room for an optical table. After some discussion, we decided that chlorine atom detection, using a tunable diode laser and the analogous transition to that discussed above in

fluorine, would be a practical experiment providing fruitful comparisons with his modeling of the plasmas. Accordingly, we have designed and assembled the necessary optical system to make such measurements and have begun laboratory studies to measure the chlorine atom absorption line strengths. These laboratory studies will permit quantitative measurement of Cl concentrations in Prof. Sawin's apparatus.

An item of considerable study and controversy in silicon/fluorine plasma etching systems has been the identity of the initial desorption products. There is evidence for at least some SiF_2 desorption, but the major final product is certainly SiF_4 , which may also be the predominant initially desorbed species. Studies of both gas phase and surface reactivities of SiF_2 will give a better idea of the role of SiF_2 as an intermediate. Workers at both Bell Laboratories (R. Gottscho) and MIT (in the group of Prof. J.I. Steinfeld) are planning experiments in which desorbing SiF_x species would be directly detected by laser induced fluorescence.

In this connection, Aerodyne is working on an NSF-funded program to study gas phase kinetics and surface reactions relevant to the fluorine/silicon plasma etching processes. Gas phase reactions of SiF_2 , CF_3 , and SiF_3 radicals with atomic and molecular fluorine, oxygen, and hydrogen will be studied. This work is complementary to the present program, in that it involves radical source development and spectroscopic characterizations which can be directed toward diagnostic measurements in plasma etching systems, as well as an improved understanding of the underlying mechanisms for these systems. The NSF program is a joint research project with Dr. Peter Gaspar of Washington University. The first systems under investigation were the gas-phase recombination of SiF_2 with F and F_2 , so that the first work done under the kinetics contract was the development of sources of SiF_2 . However, neither the infrared or ultraviolet spectroscopy of SiF_2 is as well characterized as one would like, so these were selected as areas for study.

The first application of dye laser fluorescence detection to etching or deposition systems was made only recently, with the laser induced fluorescence

detection of CF_2 in a plasma etching reactor.¹⁰ Hargis and Kushner of Sandia National Laboratories were able to correlate CF_2 concentrations with changes in the identity of the etchant gas. Although in this system a radiative lifetime is known for the electronic transition, no infrared band strengths have been measured, so we began work on the high resolution IR spectroscopy of CF_2 with that goal in mind.

Chemical vapor deposition has been used to generate a very wide variety of thin films and coatings,¹¹ and is particularly appropriate for generating the layered structures needed for advanced semiconductor devices. Chemical reactions occurring on or near a heated substrate result in the deposition of an element or compound from a feed gas. Surface reactions are thought to result in smooth, well-adhering layers, while homogeneous reactions can lead to looser deposits. Nevertheless, the gas-phase chemistry determines what molecular species arrive at the surface to participate in reactions.

In these CVD systems, in addition to the issues of structural properties and film composition, uniformity of deposition rate is a very important goal of reactor design. Spectroscopic diagnostics to determine chemical species identity and concentration are important to specify chemical mechanisms. When deposition rates are controlled by physical factors such as diffusion and flow patterns, spectroscopic diagnostics can be used to measure temperature and concentration gradients.

A simple yet very important CVD system is the pyrolysis of silane to yield deposited silicon. Silicon is by far the most important semiconductor material. The literature on the preparation of device-quality epitaxial and polycrystalline silicon is so vast as to almost defy review.¹²⁻¹³ Although much of this literature is devoted to the consideration of deposition mechanisms,¹⁴⁻¹⁵ the detailed species and processes involved are in general not known. Beyond the interest in the crystalline forms, we are now in a time of tremendous growth in interest in amorphous silicon films. Much of the interest to date has been due to solar cell applications, but more and more

microelectronics applications are now being investigated, including image pickup tubes, field effect transistors (FETs) and FET-addressed liquid crystal display panels, solid state image sensors, charge-coupled devices, optical recording, visible light emitting diodes, fast modulators and detectors, hybrid structures, memory switching, and other microelectronics applications.

Another deposition method which has been applied to a wide variety of systems and which is presently undergoing very rapid development is plasma deposition.¹⁶ Again, a chief application has been to the deposition of silicon from silane, and again there has been recent work directed towards elucidating the detailed chemical mechanisms involved.¹⁷⁻¹⁸ While most chemical vapor deposition techniques are intended to produce epitaxial, highly perfect crystalline deposits, the great interest in plasma deposition is for the production of amorphous silicon, particularly for use in solar cells. The incorporation of hydrogen into the silicon deposited in this manner results in excellent properties, while deposition uniformity is easier to control in scaling to large production facilities than it is with CVD methods. On the other hand, recent work by R. Reif at MIT has shown plasma enhanced CVD to have significant advantages in producing crystalline silicon for semiconductor devices, including spatial accuracy in doping by ion implantation.

A major problem for silicon deposition involves knowledge of the identity of the depositing species as a function of system operating parameters and the degree to which their identity influences film properties. Much kinetic modeling has made the assumptions that deposition rates at low temperatures are governed by surface reactions, and at high temperatures by diffusion to the surface.¹⁴ This means that in silane deposition SiH_4 is assumed to be the major depositing species, while in mixtures of higher silanes it is these polysilanes (or others formed in gas-phase chemistry) which decompose on the surface.

Recently, however, the importance of gas-phase chemistry which produces radicals which are much more efficient deposition species has been indicated,

both by the experimental observation¹⁹ that at low temperatures the activation energy for film growth from silane is equal to that for its gas-phase pyrolysis, and by the chemical kinetic modeling work done both at Harvard²⁰ and by a group at Sandia National Laboratories.²¹ The Sandia model employs estimated and calculated thermodynamic and kinetic parameters for SiH_2 and a variety of Si_2H_y species, and concludes that while in hydrogen carrier gas SiH_2 is the primary depositing species, in inert gas the unknown species Si_2H_2 is most important. The Harvard model includes a large series of insertion reactions involving Si_nH_{2n} diradicals and Si-H bonds in silanes to form larger polysilanes. The diradicals (the simplest being SiH_2) are formed by the reverse, dissociation process, and any diradicals which diffuse to the surface are assumed to contribute to deposition by insertion into surface Si-H bonds.

In these deposition systems, spectroscopic diagnostics are needed to specify gas phase reactant identities and concentrations, to indicate which species participate in surface reactions, and to provide spatial mapping of the plasma discharge regions.

Examples of candidate molecular radical species are those which are products of gas-phase decomposition and reaction in the silicon deposition systems from silane and chlorosilanes, such as Si, Si_2 , SiH, SiH_2 , SiCl, and HSiCl. Information on the visible spectroscopy of these molecules is often available in the literature, and a number of the smaller species have received a first study using dye laser fluorescence.

A good example is a recent study of laser induced fluorescence of silicon atoms in a radio frequency glow discharge of silane in argon.²² In other examples, members of the Sandia group detected HSiCl in vapor deposition of silicon from dichlorosilane²³ and Si_2 in silicon deposition from silane.²⁴ They measured concentration profiles over the substrate, and pointed out that the first conclusion to be drawn from their work was that these species should be included in future thermodynamic and kinetic modeling of the deposition systems.

Another species which is potentially important to monitor in silicon deposition from silanes is the SiH molecule. This species has a long history of observation in visible emission studies.²⁵⁻²⁷ Recently, SiH has been observed using an FTIR in the infrared in both emission and absorption.²⁸ Presently several groups are undertaking tunable diode laser infrared absorption studies.²⁹ To date, however, the observation method which has yielded the most information is laser induced fluorescence, in the form of a detailed study by Schmitt and co-workers³⁰ which yielded much information on the dynamics of a silane plasma. They also measured a radiative lifetime which is in good agreement with another recent measurement.³¹

Even more recent progress has been made on detection of the SiH₂ radical, which is expected to be a major component of plasma as well as thermal dissociation systems. In the recent literature, this progress has been in visible spectroscopy, both in the form of dye laser absorption spectroscopy in a glow discharge³² and a laboratory measurement of a radiative lifetime by laser induced fluorescence.³³ The absorption observation demonstrated the presence of SiH₂ in deposition-type systems in detectable amounts, but could not yield a concentration estimate since no quantitative spectroscopic information was then available. Finally, in a soon to be published paper, Hauge and co-workers³⁴ have reported matrix observations of the three infrared fundamental mode frequencies which differ completely from the previous assignments (which they suggest may at least in part be assignable to SiH₃).

Quantitative infrared spectroscopic information is available for many of the stable precursor molecules used in CVD, such as SiH₄, SiCl₄, PH₃, and so forth. An example of the application of diode laser measurements in such systems is the program at the Air Force Wright Aeronautics Laboratory for measuring SiH₄ concentrations in silane plasma discharges.³⁵ This means that, while laser induced fluorescence has a considerable advantage in its great sensitivity to some trace radical species, an infrared diagnostic system has the advantage of being able to detect both stable molecules and radicals. While, as noted above, SiH has been detected by tunable diode laser

absorption, it is typically a minor species in deposition systems. On the other hand, SiH_2 is often the major decomposition product, yet has never been observed in the infrared in the gas phase. Therefore, we targeted both band identification and line strength measurements for SiH_2 in the infrared as high priorities.

In summary, the program goals we identified during the first year were:

- o Measurement of chlorine atom densities in the plasma etching apparatus of Prof. Herbert Sawin, MIT Chemical Engineering Department, preceded by line strength measurements in our laboratory,
- o Fluorescence lifetime and quenching measurements and tunable diode laser spectroscopy of the SiF_2 molecule,
- o Quantitative tunable diode laser spectroscopy of the CF_2 molecule.
- o Tunable diode laser spectroscopy of the SiH_2 molecule.

In the following section we will describe our progress toward achieving each of these research objectives.

2. STATUS OF THE RESEARCH EFFORT

2.1 Diagnostic Measurements In a Model System

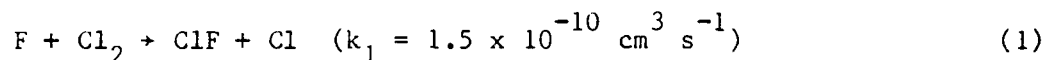
We begin our discussion of the program accomplishments during the first year with that part devoted to implementation of diagnostics to measure gas phase species or species profiles in model semiconductor fabrication devices. The goal of these measurements will be to demonstrate the application of the diagnostic techniques to measurements in a real system, to contribute to an understanding of the fabrication process under study by measurement of gas phase species present under actual operating conditions, and perhaps to assess the possible application of such on-line diagnostics to process control.

During the first year of the program, we began early to focus on identifying a model system for study. As noted above, a cooperative effort for instrumentation of an existing plasma etching system at MIT was undertaken. We had expected that the effort in the first year would concentrate on designing diagnostic adaptations for use on existing systems, and that actual diagnostic implementation and measurements would take place in the second and third years of the program. In fact, we find ourselves well ahead of that schedule, since the diagnostic system is assembled and ready to go, only awaiting the checkout which will be provided by a laboratory measurement of the chlorine atom line strength.

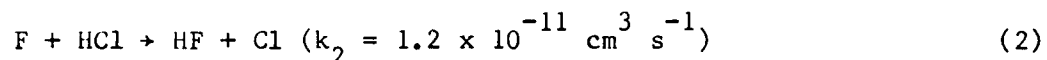
The apparatus which will be taken to MIT is composed of a diode laser, an optical table carrying a monochromator, a detector, and beam steering optics, and a multipass cell (White cell) to be placed inside the etching apparatus. The diode laser is the same one used in our laboratories in a wide variety of experiments, and will go to MIT only when the rest of the optical system is installed and aligned. All components for the optical table (including the table itself) have been purchased and assembled. The White cell mounts have

been designed and machined, and the mirrors have been purchased and coated. We have made preliminary measurements of the chlorine atom absorption lines in our laboratory discharge flow system. We are currently pursuing these measurements in order to establish the absorption line strengths, as described below.

The laboratory measurement of the chlorine atom absorption line strengths are made in our discharge-flow reactor system. Known concentrations of chlorine atoms are prepared by either of the fast reactions



or



where the fluorine atoms are produced in a microwave discharge of F_2 dilute in Ar. These sources are free of interfering secondary chemistry even at high radical concentrations ($\sim 10^{15} \text{ cm}^{-3}$), and the Cl atom concentration is simply determined by measurement of the HCl or Cl_2 flow rate (combined with measurement of the pressure and the other flows) under conditions of excess F atoms. The absorption path length is defined using an aerodynamic confinement approach and may be calibrated by comparison of absorption measurements of a stable calibration gas, carbonyl sulfide, under unconfined conditions (where the path length is the physical dimension of the cell) with measurements where the OCS is aerodynamically confined.

A spectral scan of the chlorine atom absorption lines produced by the $\text{F} + \text{Cl}_2$ reaction in our system is shown in Figure 1, along with the OCS reference lines. Hyperfine splitting of the $^2\text{P}_{1/2} + ^2\text{P}_{3/2}$ transition results in six absorption lines for each of the two Cl isotopes. The strongest line ($F = 2 + F = 3$) is coincident for the two isotopes, and this line will be utilized for

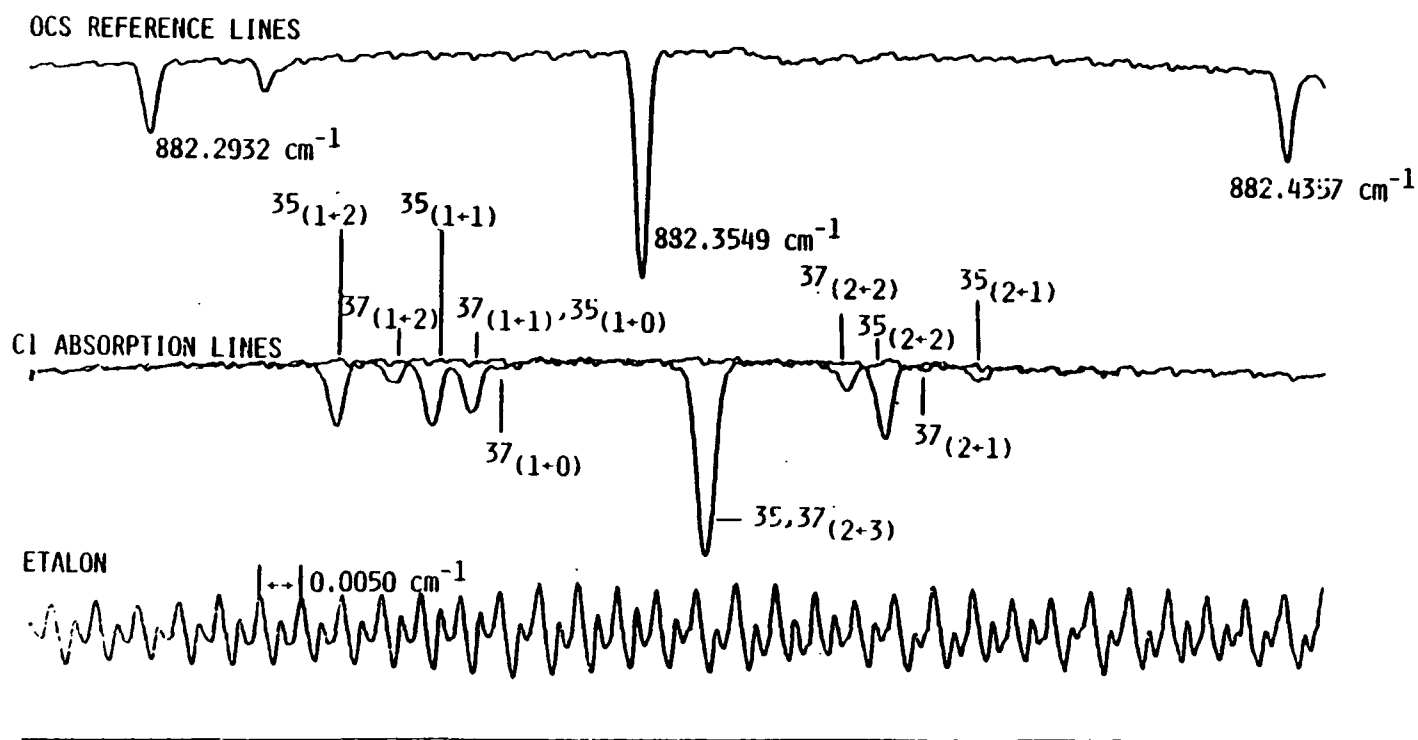


Figure 1. $^2P_{1/2} \leftarrow ^2P_{3/2}$ Absorption in Atomic Chlorine.

both the laboratory studies of line strength and the in situ diagnostic measurements in a plasma etching system. The Cl line positions as determined from the data in Figure 1, using the OCS reference lines to calibrate wavelength, are in excellent agreement with the calculated line positions based on the laser magnetic resonance data of Dagenais, et al.,³⁶ extrapolated to zero field, and the measured zero field hyperfine splittings of the $^2P_{3/2}$ and $^2P_{1/2}$ levels.³⁷⁻³⁸ In the MIT apparatus, we expect 10^{14} cm^{-3} or more Cl atoms, while our detection limit will be around $2 \times 10^{12} \text{ cm}^{-3}$.

In addition to beginning collaboration on an etching system diagnostic with Prof. Sawin, we discussed diagnostics possibilities in the plasma-assisted chemical vapor deposition systems of Prof. Rafael Reif of the MIT Electrical Engineering department. One apparatus with definite possibilities for useful application of optical diagnostics is used to deposit titanium silicide from SiH_4 and TiCl_4 at 50-100 mTorr, while a second apparatus is used with 10-20 mTorr SiH_4 to study arsenic autodoping.

Another possible cooperative effort could involve a program at Aerodyne to study chemical vapor deposition processes, under funding by NASA. As part of this program, Aerodyne has constructed an inductively-heated horizontal reactor of the type used in epitaxial CVD growth. This reactor includes windows to permit optical access for spectroscopic diagnostics. The intent of the NASA program is to study CVD growth of crystalline silicon thin films by pyrolysis of SiH_4 under controlled conditions of variable buoyancy in the carrier gas/feed gas flow. The availability of this apparatus may allow us to test and perform diagnostics under the AFOSR program which complement the NASA study or which extend the study to other CVD processes. The NASA study is a joint project with Dr. Karl Spear of Pennsylvania State University.

In the course of our work on the project, we will continue to maintain close interaction with other workers. In addition to the academic associations described above, we have consulted with Prof. J.I. Steinfeld of MIT, Prof. R.G. Gordon of Harvard, Prof. P.P. Gaspar of Washington University, St. Louis, and Prof. F. Kaufman of the University of Pittsburgh, as well as

interfacing with researchers in various government-funded and industrial laboratories, including Bell Laboratories, IBM, Xerox Palo Alto Research Center, Air Force Wright Aeronautical Laboratories, NASA Lewis Research Center, and others.

2.2 Laboratory Spectral Studies

Now we turn to progress to date in laboratory measurements of quantitative spectroscopy of radical species. These studies are performed in order to develop a base of sufficient spectroscopic data to support optical diagnostics. A little more than a year ago, we presented a review of the capabilities of laser diagnostics in etching and deposition systems.³⁹ The review focused on the use of tunable infrared diode lasers and tunable visible/ultraviolet dye lasers, and included descriptions of the apparatus and its operation for each technique. Also included in that review were estimates of minimum detectable densities for a wide range of pertinent species, based on quantitative spectroscopic data when they were available and estimated when they were not. In the ensuing year, work in our laboratory and a number of papers appearing in the literature have resulted in additional basic data becoming available, so that our original paper required an update.⁴⁰ In this section on progress on selected molecules, we will note several such instances.

As noted above, our spectroscopic studies of the SiF_2 radical have benefited from source development undertaken as part of an NSF program which focuses on measuring selected reaction rates of radicals expected in fluorine/silicon plasma etching systems. The three radicals selected as being most important to include in these studies were SiF_2 , CF_3 , and SiF_3 , with SiF_2 being studied first. A subcontract to Washington University, St. Louis is devoted to development of sources for these radicals. The kinetic studies are conducted utilizing the same fast-flow reactor facilities and laser induced fluorescence and long path diode laser absorption spectroscopic species detection techniques as are the spectroscopic studies done under this program.

Spectroscopic detection of SiF_2 by either diode laser infrared absorption or ultraviolet resonance fluorescence had never been done before. Therefore, demonstration of either technique is of great interest for possible application as a diagnostic in laboratory plasma etching systems or in experiments which model some part of that process. On the other hand, a good foundation exists in the form of conventional spectroscopy of both the vibrational and electronic bands. Finally, another reason for developing a good spectroscopic detection method was to give unequivocal evidence of SiF_2 generation from any source used in the kinetics program, since development of new sources was a major thrust of that program.

As a novel source of SiF_2 , we had proposed the thermal decomposition of Si_2F_6 . In contrast to the standard method of passing SiF_4 gas over hot silicon,⁴¹ we felt it offered the benefits of being a homogeneous, easily controlled reaction, generating a fixed ratio of SiF_2 and SiF_4 , without significant concentrations of interfering radicals. Several samples of Si_2F_6 were synthesized at Washington University and shipped to Aerodyne.

However, the initial spectroscopy and kinetics studies used the hot Si/SiF_4 method, already proven to produce large quantities of SiF_2 , although with some potential drawbacks. An existing Aerodyne tube furnace was refitted with heating elements capable of operation in the 1150 to 1250°C range required for SiF_2 production. Indeed, a strong diode laser infrared absorption spectrum was observed at furnace temperatures above 1100°C, which increased dramatically with increasing temperature but otherwise remained unchanged. An example is shown in Figure 2. Comparison is underway between this complex, many line spectrum and an existing lower resolution FTIR spectrum of the ν_1 and ν_3 stretching modes of SiF_2 .⁴² A rough estimate of flow tube SiF_2 concentration implies an infrared minimum detectable density up to 20 times higher than that estimated in Ref. 39. Again, we plan a precise infrared band strength measurement either by comparison to ultraviolet absorption (here an oscillator strength measurement will also be required) or by chemical conversions which quantify the SiF_2 concentration. To this end, we have begun laser fluorescence measurements, as detailed below.

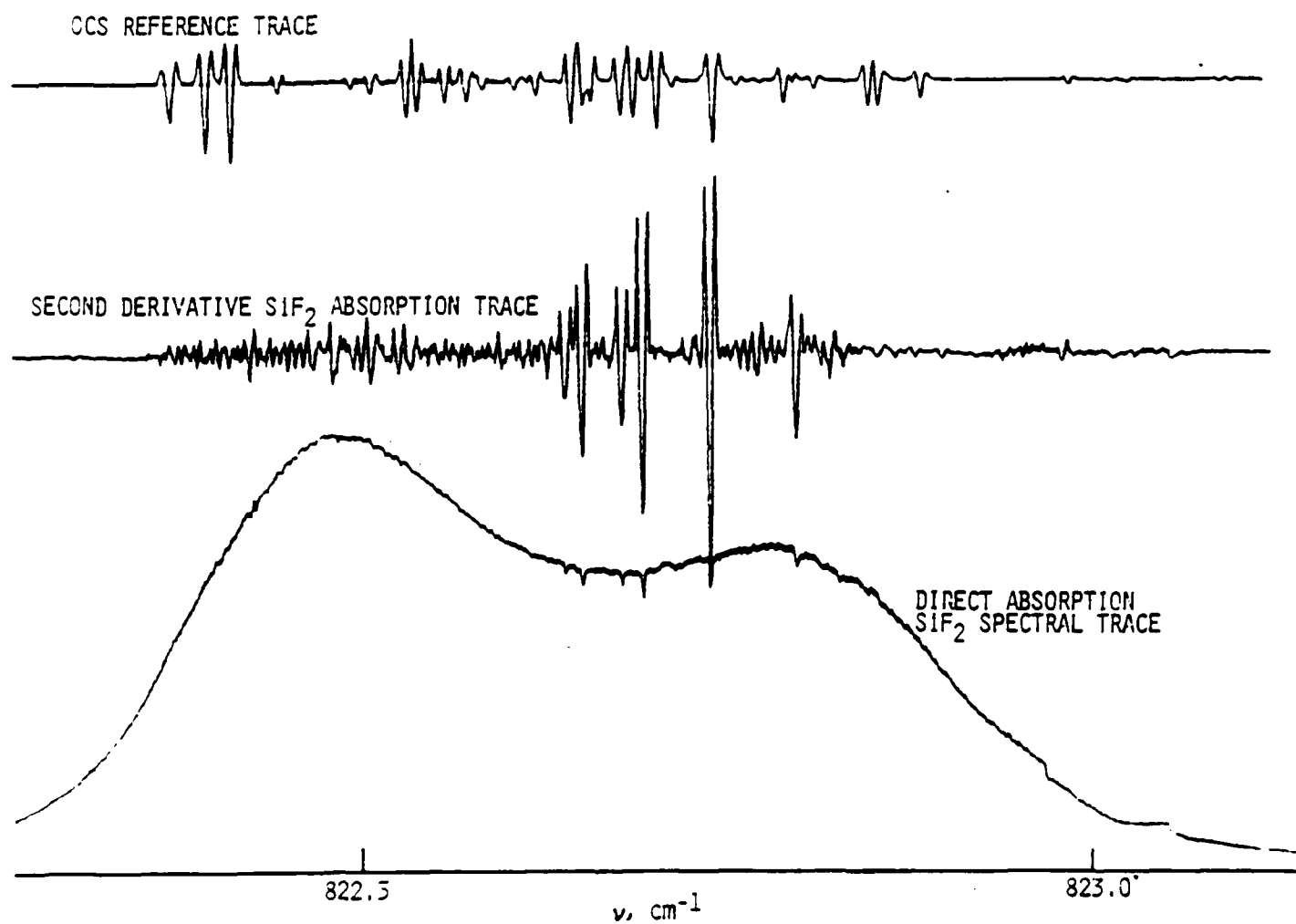


Figure 2. SiF₂ Tunable Diode Laser Infrared Absorption Spectrum. OCS₂ Reference Lines Provide an Absolute Frequency Scale (Line Listings Received from A. Maki of NBS).

As part of the kinetics studies we investigated both an alternate source of SiF_2 (thermal decomposition of Si_2F_6) and an alternate detection method (UV laser induced fluorescence in the A-X band system). The Si_2F_6 , entrained in a carrier flow of helium, was heated in a quartz tube with the same external oven used in the SiF_4/Si source. SiF_2 was detected with the diode laser for oven temperatures greater than 700°C . For temperatures in the range of 800°C to 1200°C , this source appeared to have about the same efficiency of SiF_2 production as the SiF_4/Si source at 1200°C .

Laser induced fluorescence (LIF) using the output of a doubled nitrogen-pumped tunable dye laser resulted in greatly improved detection sensitivity compared with infrared absorption. The laser excitation spectrum showed prominent intensity peaks which corresponded with the vibrational band structure previously observed in absorption.⁴³ An example is shown in Figure 3. Some time-resolved studies of radiative decay rates were also made. Fluorescence decays on several different time scales were observed to be superimposed. The slowest decay ($\sim 6 \mu\text{sec}$) was rapidly quenched (gas kinetic rates were indicated) by both helium and argon carrier gas. Therefore, this component does not contribute under the conditions used to measure reaction rates (2-10 Torr). An intermediate decay of $\sim 150 \text{ nsec}$ was also observed. The fastest decay of less than 60 nsec provided greater than 95% of the total signal. A radiative lifetime of this magnitude for SiF_2 is not unreasonable in that a value for CF_2 of 59 nsec has been measured.⁴⁴ The existence of multiple lifetimes can be explained by several mechanisms; it should be noted that the lifetime behavior was not observed to change with shifting excitation wavelength, indicating that the presence of more than one chemical species was not a likely cause. Further clarification requires single vibronic state resolution of the induced fluorescence. Further studies in this area are anticipated.

With LIF shown to be an adequate detection method to determine relative concentrations of SiF_2 , we proceeded to flow tube chemical kinetics studies. We also attempted diode laser observations of the products of discharging

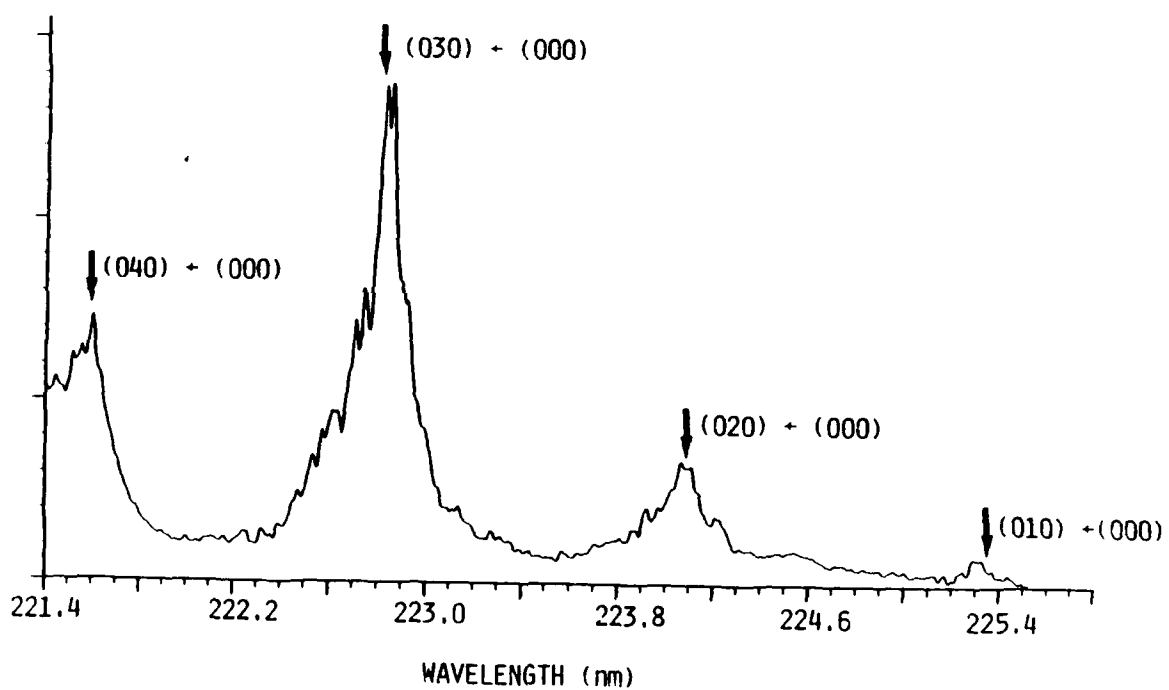


Figure 3. SiF₂ Fluorescence Excitation Spectrum
(Arrows Denote Band Positions from Ref. 43)

SiF_4 , but this resulted in no detectable SiF_2 absorption (and no absorption by SiF , which lies in the same spectral region). This failure was somewhat surprising considering the ease with which diode laser spectra of CF_2 were obtained using a microwave discharge and CF_4 as a source. An example of the CF_2 spectrum, done recently at Aerodyne this program, is shown in Figure 4.

Since there has been particular speculation on the role of CF_2 in etching chemistry, diode laser measurements of its infrared spectrum could support very useful quantitative diagnostic. Using the discharge formation method, the same as that of Davies and co-workers,⁴⁵⁻⁴⁶ we have verified positions for some of the ν_3 band lines observed by them and added some additional lines. A band strength measurement is of most interest to further quantitative studies, since only theoretical values are available for both CF_2 and CF_3 .⁴⁷ Since discharge formation is not quantitative and the products can vary with source gas and discharge parameters, we plan ultraviolet absorption measurements, with perhaps a thermal dissociation source as a check.

Finally, we are actively pursuing the development of SiH_x diagnostic measurements for use in deposition systems. Our initial work has focused on tunable diode laser studies of the infrared spectra of SiH_x radicals. The potential for high accuracy and line of sight spatial resolution, combined with the ability to study both radical and stable species make this an attractive alternative diagnostic to laser fluorescence. The first requirement for these studies is a radical source in which radicals are not immediately lost to deposition. Although we plan to eventually use our high temperature flow tube in conjunction with a thermal decomposition source, the first source to yield results has been the reaction of fluorine atoms with silane. Figure 5 shows a spectrum in the vicinity of a pair of SiH lines, together with the various reference gas lines which accurately determine line positions. The SiH absorption intensity shows first a growth and then a decay as the F atom concentration is increased relative to the initial silane concentration.

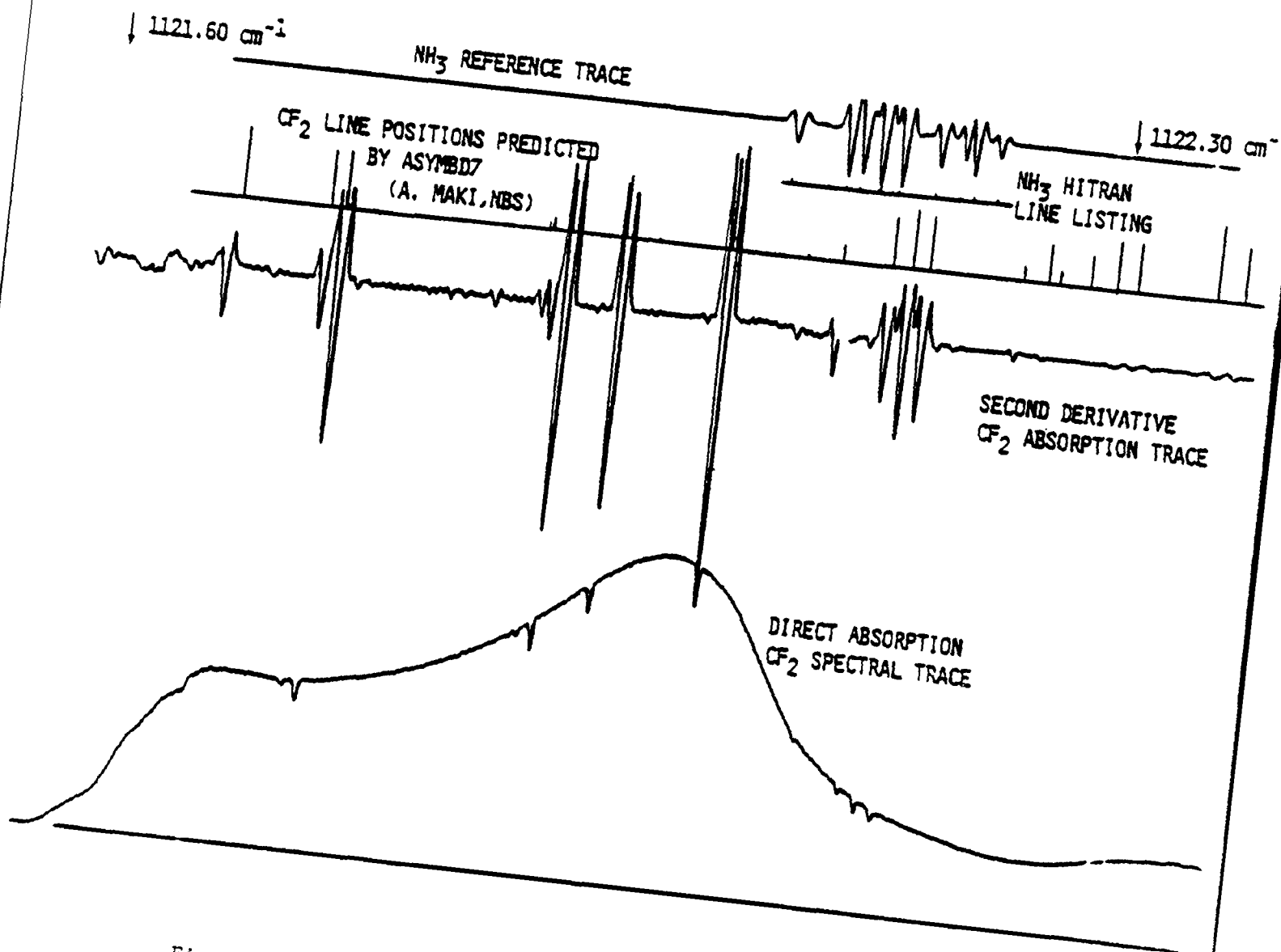


Figure 4. CF_2 Tunable Diode Laser Infrared Absorption Spectrum.

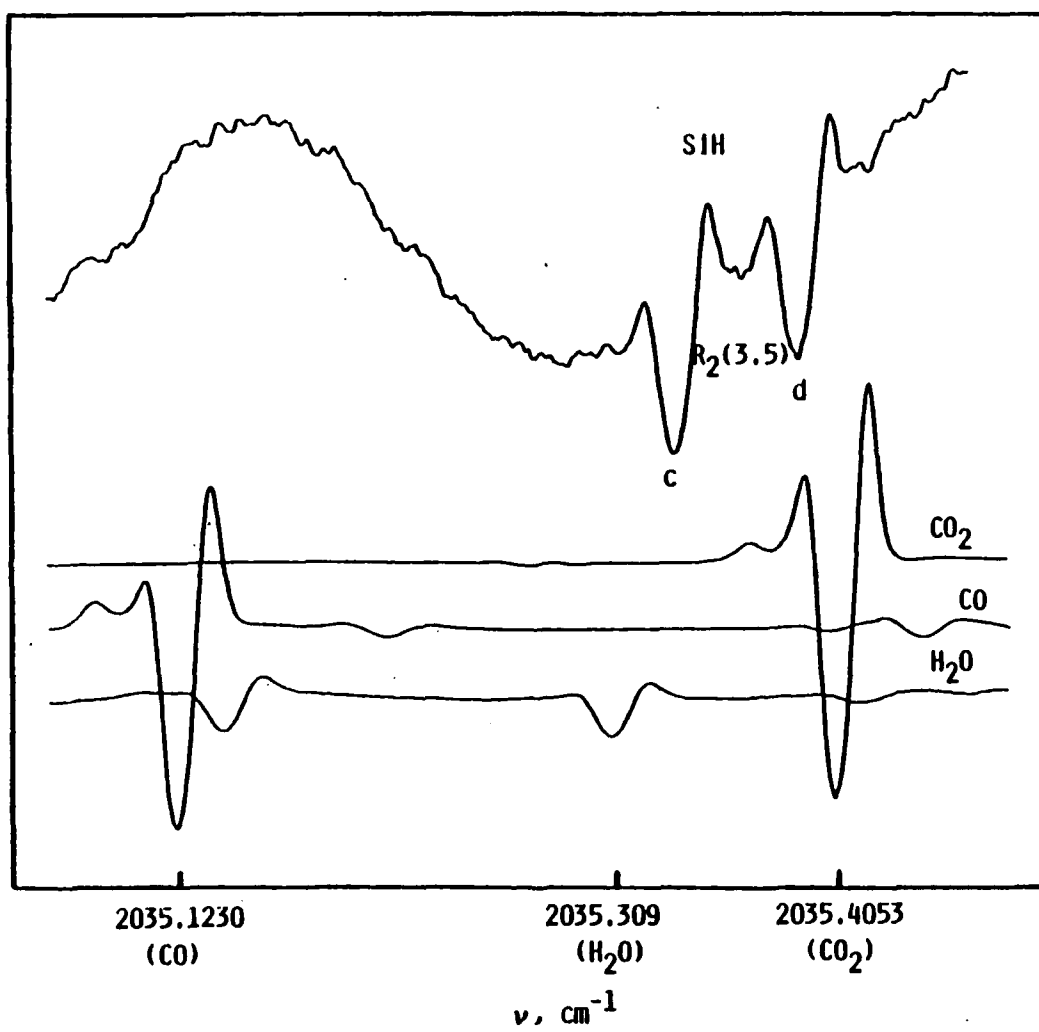


Figure 5. Absorption Spectrum of SiH.

Additional absorption lines are detected, with intensities that vary with the F atom concentration in a manner characteristic of an SiH_x species with x greater than one. Figure 6 shows the appearance and disappearance of some of these peaks. They are tentatively marked SiH_2 , because matrix isolation spectroscopy available at that time⁴³ indicated a band in this region; however, a more reliable assignment from recent matrix isolation studies³⁴ now suggests the SiH_2 band is at lower frequency, with a center perhaps around 2000 cm^{-1} . These workers also suggest that the band we observe may be due to SiH_3 .

Our efforts to observe SiH_2 visible fluorescence in this system have been thwarted by the strong background chemiluminescence to be expected in such systems from one or more reactions.⁴⁹ Therefore, this check will have to await another source, such as a thermal decomposition method. Recent LIF measurements³³ on SiH_2 have shown its radiative lifetime to be considerably shorter than that estimated in Ref. 39, implying an even smaller minimum detectable density. If the lines seen in Figure 6 were confirmed to be SiH_3 , this would be the first observation in the gas phase in this spectral region. If the SiH_2 bands could also be found at lower frequency, these also would be first observations. We have obtained some Si_2H_6 from Prof. Gaspar's laboratory, which should thermally dissociate under more moderate temperature conditions than SiH_4 .

2.3 Second Year Research Plan

During the second year of the program, we plan to complete the preliminary laboratory measurements on atomic chlorine and proceed with the in situ measurements of Cl in Prof. Sawin's plasma etching research apparatus at MIT. We also plan to continue our studies of the quantitative spectroscopy of the other radicals discussed in this section, with special emphasis on characterizing the IR spectra of gas phase SiH_x species.

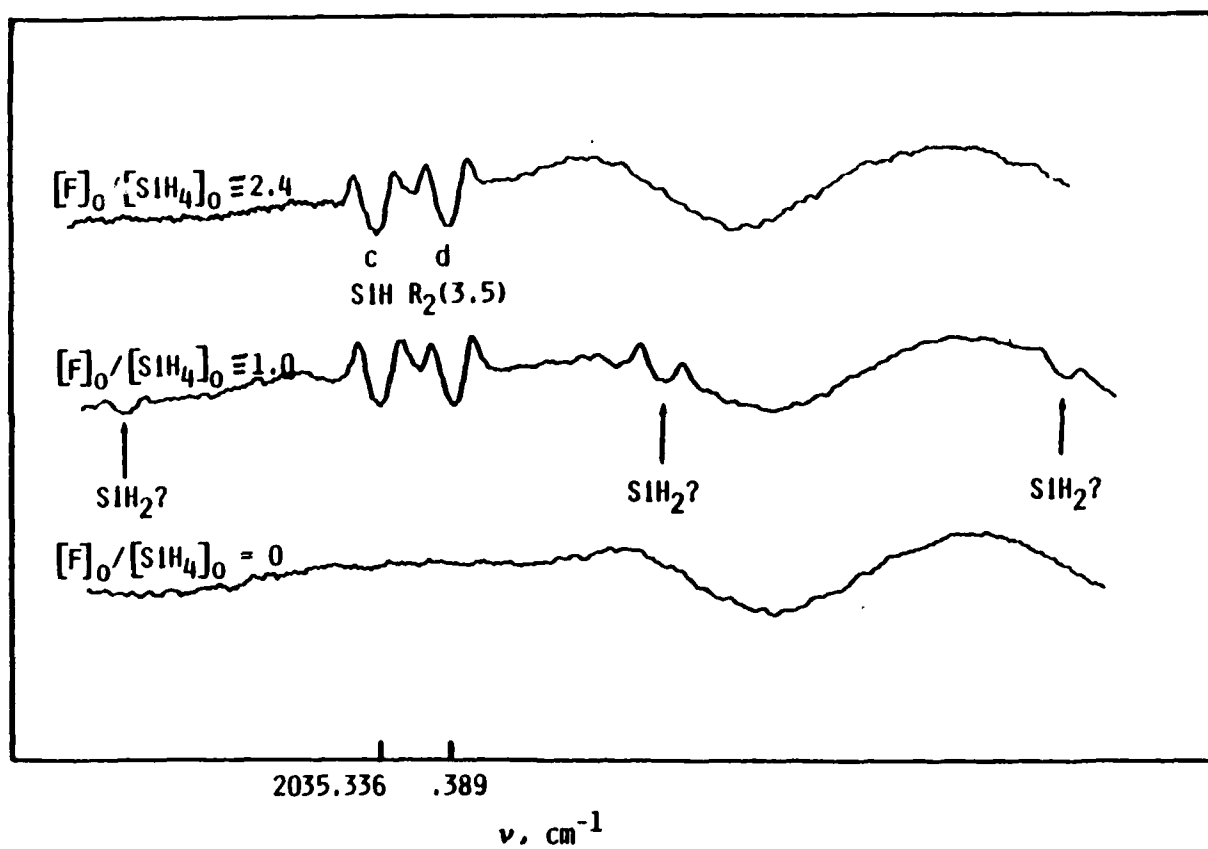


Figure 6. Absorption Features Near 2035 cm⁻¹ in Low Pressure Silane - Atomic Fluorine Reaction Zone.

3. PUBLICATIONS

Written publications:

J. Wormhoudt, A. Stanton, and J. Silver, "Laser Diagnostics of Semiconductor Processing Systems," Paper presented at 1984 Materials Research Society Symposium on Plasma Synthesis and Etching of Electronic Materials, Boston, November 16-30, 1984.

Manuscripts in preparation, planned for later submission:

A.C. Stanton and J. Wormhoudt, "Line Strength of the Atomic Chlorine $^2P_{1/2} + ^2P_{3/2}$ Spin Orbit Transition."

Work on in situ measurement of chlorine atom concentrations in etching systems as well as on SiF_2 , CF_2 , and SiH_2 spectroscopy is not sufficiently advanced to identify likely titles with any certainty.

4. PERSONNEL

Professional personnel directly associated with the research were the principal investigators, Drs. Joda Wormhoudt and Alan C. Stanton.

5. INTERACTIONS

In addition to the Materials Research Society paper noted above, which was presented by Dr. Stanton and will also be published, the following meetings were attended. In all cases a presentation was made. (The name of the presenter is given in parentheses.)

Gordon Research Conference on Plasma Chemistry, Tilton, NH, August 13-17, 1984 (Wormhoudt).

37th Annual Gaseous Electronics Conference, Boulder CO, October 9-12, 1984 (Stanton).

National Silicon Carbide Review Meeting, Raleigh, NC, November 27, 1984 (Wormhoudt).

Gordon Research Conference on Chemistry and Electronic Materials, Santa Barbara, Calif, February 18-22, 1985 (Wormhoudt).

ACS Conference on Chemistry of Microcircuit Fabrication, Lexington, MA, April 3, 1985 (Stanton).

6. REFERENCES

1. B. Chapman, Glow Discharge Processes, John Wiley, Somerset, NJ, 1980.
2. D.L. Flamm and V.M. Donnelly, Plasma Chemistry and Plasma Processing 1, 317 (1981).
3. J.W. Coburn and H.F. Winters, Ann. Rev. Mater. Sci. 13, 19 (1983).
4. J.W. Coburn, "Plasma Assisted Etching", in Proceedings of the Tutorial Symposium on Semiconductor Technology, D.A. Doane, D.B. Fraser, and D.W. Hess, Eds., The Electrochemical Society, Pennington, NJ, 1982, p. 177.
5. D. Edelson and D.L. Flamm, J. Appl. Phys. 56, 1522 (1984).
6. M.J. Kushner, J. Appl. Phys. 53, 2923 (1982).
7. J.A. Mucha, D.L. Flamm, and V.M. Donnelly, J. Appl. Phys. 53, 4553 (1982).
8. A.C. Stanton and C.E. Kolb, J. Chem. Phys. 72, 6637 (1980).
9. A.C. Stanton, J.C. Wormhoudt, and J.W. Duff, in Spectral Line Shapes, Vol. 2 (Walter de Gruyter and Co., New York, 1983), pp. 515-529.
10. P.J. Hargis and M.J. Kushner, Appl. Phys. Lett. 40, 779 (1982).
11. W.A. Bryant, J. Mat. Science 12, 1285 (1977).
12. W. Kern and V.S. Ban, "Chemical Vapor Deposition of Inorganic Thin Films," in Thin Film Processes, Ed. J.L. Vossen and W. Kern, Academic Press, New York, 1978, p. 257.
13. D.T. Hawkins, Chemical Vapor Deposition, 1960-1980, Plenum, New York, 1981.
14. J. Bloem and L.J. Giling, "Mechanisms of the Chemical Vapor Deposition of Silicon," in Current Topics in Materials Sciences 1, Ed. E. Kaldis, North-Holland, Amsterdam, 1978, p. 147.
15. W.A.P. Claasen and J. Bloem, Philips J. Res. 36, 124 (1981).
16. S. Veprek, "Applications of Low Pressure Plasmas in Materials Sciences: Especially Chemical Vapour Deposition", in Current Topics in Materials Science, Vol. 4, Ed. E. Kaldis, North-Holland, p. 151 (1980).

17. R. Robertson, D. Hils, H. Chatham, and A. Gallagher, Appl. Phys. Lett. 43, 544 (1983).
18. F.J. Kampas and R.W. Griffith, Appl. Phys. Lett. 39, 407 (1981).
19. A.M. Beers and J. Boleno, Appl. Phys. Lett. 41, 153 (1982).
20. F.B. Ellis, Jr., Thesis, Harvard University, 1983.
21. M.E. Coltrin, R.J. Kee, and J.A. Miller, J. Electrochem. Soc. 131, 425 (1984).
22. R.M. Roth, K.G. Spears, and G. Wong, Appl. Phys. Lett. 45, 28 (1984).
23. P. Ho and W.G. Breiland, Appl. Phys. Lett. 43, 125 (1983).
24. P. Ho and W.G. Breiland, Appl. Phys. Lett. 44, 51 (1984).
25. J. Perrin and E. Delafosse, J. Phys. D. 13, 759 (1980).
26. S. Yokoyama, M. Hirose, and Y. Osaka, Jap. J. Appl. Phys. 20, L117 (1981).
27. M. Hirose, T. Hamasaki, Y. Mishima, H. Kurata, and Y. Osaka, in Tetrahedrally Bonded Amorphous Semiconductors, Ed. R. A. Street, K.K. Biegelsen, and J.C. Knights, AIP Conference Proceedings No. 73, 1981.
28. J.C. Knights, J.P.M. Schmitt, J. Perrin and G. Guelachvili, J. Chem. Phys. 76, 3414 (1982).
29. P. Chollet, G. Guelachvili, and M. Morillon, Bull. Soc. Chim. Belges 92, 512 (1983).
30. J.P.M. Schmitt, P. Gressier, M. Krishnan, G. deRosny and M. Perrin, Chem. Phys. 84, 281 (1984).
31. W. Bauer, K.H. Becker, R. Duren, C. Hubrich, and R. Meuser, Chem. Phys. Lett. 108, 560 (1984).
32. J.M. Jasinski, E.A. Whittaker, G.C. Bjorklund, R.W. Dreyfus, R.D. Estes, and R.E. Walkup, Appl. Phys. Lett. 44, 1155 (1984).
33. G. Inoue and M. Suzuki, Chem. Phys. Lett. 105, 641 (1984).
34. L. Fredin, R.H. Hauge, Z.H. Kafafi, and J.L. Margrave, J. Chem. Phys. 82, (8), in press.

35. C.A. DeJoseph, Jr., A. Garscadden, and D.R. Pond, Proceedings of the International Conference on Lasers '82, New Orleans, LA, (December 1982), STS Press, McLean, VA (1982).
36. M. Dagenais, J.W.C. Johns, and A.R.W. McKellar, Can. J. Phys. 54, 1438 (1976).
37. V. Jaccarino and J.G. King, Phys. Rev. 83, 471 (1951).
38. J.G. King and V. Jaccarino, Phys. Rev. 84, 852 (1951).
39. J. Wormhoudt, A.C. Stanton, and J.A. Silver, Proc. SPIE 452, 88 (1984).
40. J. Wormhoudt, A. Stanton, and J. Silver, "Laser Diagnostics of Semiconductor Processing Systems," Paper presented at 1984 Materials Research Society Symposium on Plasma Synthesis and Etching of Electronic Materials, Boston, November 16-30, 1984.
41. J.L. Margrave and P.W. Wilson, Accounts Chem. Res. 4, 145 (1971).
42. G.L. Caldow, C.M. Deeley, P.H. Turner, and I.M. Mills, Chem. Phys. Lett. 82, 434 (1981).
43. V.M. Khanna, G. Besenbruch, and J.L. Margrave, J. Chem. Phys. 46, 2310 (1967).
44. F.B. Wampler, J.J. Tise, W.W. Rice, and R.C. Oldenburg, J. Chem. Phys. 71, 3926 (1979).
45. P.B. Davies, P.A. Hamilton, J.M. Elliot, and M.J. Rice, J. Mol. Spec. 102, 193 (1983).
46. P.B. Davies, W. Lewis-Bevan, and D.K. Russell, J. Chem. Phys. 75, 5602 (1981).
47. J.H. Newton and W.B. Person, J. Chem. Phys. 68, 2799 (1978).
48. D.E. Milligan and M.E. Jacox, J. Chem. Phys. 52, 2594 (1970).
49. C.P. Connor, G.W. Stewart, D.M. Lindsay, and J.L. Gole, J. Am. Chem. Soc. 99, 2540 (1977).